64499

Dechlorination of PCBs in Sediments of New Bedford Harbor

James L. Lake, Richard J. Pruell, and Frank A. Osterman

U.S. Environmental Protection Agency
Environmental Research Laboratory-Narragansett
South Ferry Road
Narragansett, RI 02882

August 30, 1989

New Bedford
11.12
64499

## Abstract

The distributions of PCBs in New Bedford Harbor Superfund Site (NBHSS) sediments showed considerable compositional alterations relative to (1) inputs of Aroclor 1242 and 1254 standards, and (2) distributions present in sediments from lower New Bedford Harbor and Black Rock Harbor, CT. The compositional alterations, which presumably result from reductive dechlorinations by bacteria, became more extensive with decreasing distance from the Aerovox Plant (which is suspected as the source), and increasing sediment PCB concentrations. The most extensively altered PCB distribution was found in the 6 to 7 inch deep section of a core from nearest the plant's outfall, and less altered PCB residues were found in the upper (0-1 and 2-3 inch) core sections. The dechlorinating bacteria appear to preferentially attack the potentially toxic coplanar and mono-ortho substituted congeners and, therefore, these processes may decrease the potential toxicity of these residues. Estimates of the rates of the dechlorination processes showed considerable variability depending on the congener and the sediment sample.

## Introduction

The breakdown of PCB congeners *in situ* in sediments heavily contaminated with PCBs by processes called reductive dechlorinations have been reported (Brown et al., 1984; Brown et al., 1987(a); Brown et al., 1987(b)). These studies characterized several distinct dechlorination patterns, caused by different strains of anaerobic bacteria, which resulted in PCB residues that were altered from the original Aroclor inputs. In the area designated as the New Bedford Harbor Superfund site (NBHSS) which was heavily contaminated by Aroclor 1254 (used from 1947-1963) and Aroclor 1242 (used from 1963-1970) releases from a capacitor plant, the dechlorination patterns have been designated H and H' (Brown and Wagner, 1986). The alterations in PCB residues which occur as a result of pattern H and H' dechlorinations in 2-3 inch and 6-7 inch sections of cores taken in the Northern part of the NBHSS near the plant outfall have been documented (Brown and Wagner, 1986). However, sediment core sections taken in the Southern part of the NBHSS as part of an experimental dredging project and analyzed by ERL-Narragansett showed no clear evidence of dechlorinations in 0-6, 6-12 and 12-18 inch core sections. The present study was undertaken to determine the extent to which dechlorination processes were occurring in the NBHSS so knowledge of those processes could be incorporated into evaluations of proposed remediation of the site.

## Methods

Sediment cores were collected by piston corer in the New Bedford Harbor Superfund Site (NBHSS) and Lower New Bedford Harbor (LNBH) during the period July 5-7, 1988, at the locations shown (Figure 1, Table 1). Cores were capped and placed inside sealed plastic bags. The cores were stored in water ice shortly after collection and during the transport to the ERLN (EPA-Narragansett) and then frozen (-20°C) at ERLN. From collection to the time they were frozen, cores were held vertically to avoid mixing of sediment layers. Samples of core sections were taken from frozen cores using a power drill and a one-inch diameter hole saw to cut a plug from the cores at the desired depths. The hole saw used for sampling was washed in a soap and water solution followed by washing in acetone between cuttings to avoid cross contamination of samples. The depths of sediment sections were taken in inches to facilitate comparison with other work (Brown and Wagner, 1986). Core sections were taken at 0-1, 2-3, 6-7, 12-13, 18-19, and 24-25 inches, but in shorter cores only the top sections could be sampled. The core section samples were extruded into precleaned glass jars, capped and stored at -20°C until analysis.

The sediment sample from Black Rock Harbor, CT, was part of a large collection of sediment dredged from the Harbor and used in the joint EPA Corps of Engineers Field Verification Project (Lake et al., 1985).

## Analytical Methods

Core sections were thawed, mixed thoroughly with a stainless steel spatula and a weighed aliquot was dried in a dessicator to constant weight to determine sediment water content. A one gram aliquot of the wet sediment was extracted with five ml of acetone for 30 seconds using an Ultrasonic Probe (Model W-370) Heat Systems - Ultrasonics Inc.[1] The sample was centrifuged to separate the phases and the acetone extract was saved. The extraction was repeated, and the extracts combined. Five ml of deionized water were added to the combined acetone extracts along with one ml of heptane. The sample extract was shaken for 30 seconds and centrifuged to separate the layers. The heptane extract was removed and reacted with 1 ml concentrated $H_2SO_4$. The heptane layer was removed and reacted with reduced copper powder to remove elemental sulfur and then analyzed for PCBs.

Sediment extracts were analyzed for PCBs on a Hewlett-Packard 5890A gas chromatograph equipped with a splitless injection port, electron capture detector and a 60 meter fused silica column coated with a 0.25 micron coating of DB-5 (J+W Scientific, Inc.). The injector temperature was 270°C and the detector temperature was maintained at 315°C. The column was held at 150°C for one minute following injection then programmed to 290°C at 1°C/minute and held at 290°C for five minutes. The output from the detector was collected on a Perkin Elmer LIMS

[1] Mention of product names does not constitute endorsement by the U.S. EPA.

3210 computer.

Due to the high concentrations of extracts, they were diluted prior to GC analysis with measured amounts of heptane containing octachloronaphthalene (OCN). The OCN served as an internal injection standard for peak identification.

The congeners comprising a peak were identified by injections of individual congener standards. For peaks for which standards were not available, identifications were based on literature values (Brown and Wagner, 1986; Schultz et al., 1989). Selected peaks were eliminated from analysis because their distorted peak shape (due to coelution of numerous congeners) resulted in ambiguities in their identification and quantitation. Other peaks which are only very minor constituents of A-1242 and A-1254 also were eliminated from analysis. The peaks utilized in this study, the corresponding congeners, and the method of identification are shown (Table 2).

Quantitation of concentrations was done using external standards of A-1242 and A-1254. Spike and recovery tests of the procedure showed an average recovery of 106.3% (S.D. 23.7%) for individual peaks present in a mixture of Aroclor standards. Results were not corrected for recovery efficiencies. Blanks were processed with sample sets and showed no contamination which interfered with analysis of PCBs examined.

A computer program was developed to calculate the percentages of A-1242 and A-1254 content of samples from this study. This program used peak P039B as representative of A-1242 and peak P061 as representative of A-1254. These peaks were selected as representative of the Aroclor mixtures because they were found to be the most resistant to changes as a result of dechlorinations in this, and another study (Brown and Wagner, 1986). Since these peaks are both present in A-1242 and A-1254 the computer program does a series of successive approximations and corrections to determine the concentrations and percentage mixture of Aroclors in the residue. These data were used with relative concentration data from A-1242 and A-1254 standards to reconstruct the original composition of the PCB mixtures which contaminated a specific sediment sample. The heights of peaks calculated to be in these original mixtures are called predicted values and are compared with measured values obtained from analyses of extracts from sediment samples. Comparative abundance plots (CAPs) are used to show the measured abundances (the abundance of congener X extracted from a sediment) relative to the predicted abundance (the abundance of a congener X in the mixtures which contaminated a specific sediment) and thereby show changes in PCB residues which have occurred since impact.

## Results and Discussion

The results of sediment analysis showed that PCB concentrations increased from South to North in the New Bedford Harbor Superfund Site (NBHSS), and the highest concentrations were found nearest the Aerovox capacitor plant (Figure 1, Table 3). In surface core sections (0-1") within the superfund site

(SS) PCB concentrations as total of A-1242 and A-1254 ranged from 102 ppm to 912 ppm. Surface sections of cores C6 and C7 from lower New Bedford Harbor (LNBH) had lower concentrations, 2.1 and 9.4 ppm, respectively. The sediment sample from Black Rock Harbor, CT, contained 21.4 ppm PCBs.

Concentrations in cores from the SS generally increased with depth to the 6-7 inch section then decreased rapidly in lower core sections. The highest concentration (2,970 ppm) was found in the 6-7 inch section of Core I11. Core C7 from LNBH showed about the same PCB concentration (9.4-7.4 ppm) in sections from 0-1 to 12-13 inches. Core C6 and Core H26 contained only trace amounts (< 0.2 ppm) of PCB in sections deeper than 0-1 inches (C6) and 2-3 inches (H26).

In some cores from the SS the percentage composition of A-1242 and A-1254 changed with depth. Cores I11 and H22 showed a relative increase in the percentage of A-1254 at the 6-7 inch section. Core I14 showed a similar change at the 12-13 inch section, but Core H17 showed little change in the percentage Aroclor composition with depth. A small relative increase in the A-1254 composition was observed in the 2-3 inch section of core H26. The increases in percentage composition of A-1254 observed in lower core sections may reflect the history of inputs of Aroclor mixtures to the SS. Prior to 1963, the inputs are believed to be predominantly A-1254, from 1963 to 1970 A-1242 was used and from 1970 to 1979, A-1016 was used (Plant Records, 1985). The fact that Aroclor mixtures change differently from core to core and the presence of A-1242 and A-1254 at all depths probably result from differences in depositional rates and/or percolation of PCB mixtures into the sediments. These results indicate that a historical record of PCB inputs to the SS is not well preserved in some cores and underscores the difficulty in attempting to estimate rates of processes based on sedimentation rates. Core C7 shows a percentage composition of A-1242 and A-1254 which is lower in A-1242 and higher in A-1254 than found in the SS cores. The percentage composition of this core is about 38% A-1242:65% A-1254 for the top sections, but changes to 51% A-1242:49% A-1254 at the 12-13 inch section. This NBH core is located just inside the Hurricane Barrier and may have received inputs from sources other than the one that contaminated the SS.

Substantial changes in the relative distributions of PCB congeners which appear to be due to reductive dechlorinations were found in many samples from the SS, but samples from LNBH and BRH showed only small alterations. Comparisons of the relative distributions of PCBs were made using chromatograms of extracts and using comparisons of the abundances of congeners in a sample with those present in the original mix of Aroclor which were input to the particular sediment sample. The comparative abundance plots (CAPs) are particularly useful, because they readily show which peaks are changing relative to the original inputs and are therefore useful to identify peaks which changed as a result of environmental processes. CAPs for a mixture of A-1242 and A-1254 (53:47) standards for core sections H2267, and

I1167 and for the BRH sediment are shown (Figure 2). CAPs for the mixture of Aroclor standards showed only small changes between the predicted and measured abundances. For the H2267 core section the bars to the left showed measured abundances which were below predicted values (less than zero) (Figure 2). These bars represent peaks containing congeners which are of relatively low molecular weight and are more volatile and more soluble than most of the other PCBs present. The decreased abundance of these congeners probably result from evaporative and/or dissolution losses of these congeners prior to incorporation into consolidated sediment. At higher molecular weights, peaks CB072, P044, P055, CB179 and P088 show measured values which are two or more times greater than the predicted values. These peaks also increase in the sample from BRH and therefore may not be indicative of dechlorination processes. Notable decreases in the relative abundances of peaks P058, CB085, CB132 and CB105 are shown in the CAP for H2267, but similar decreases in the relative abundance of these peaks in the CAPs for BRH or for core C7 from Lower NBH were not observed. In the most highly dechlorinated samples I1167 (Figure 2c), the above peaks as well as other peaks (e.g., CB031, P045, P046, P047, P048, P053, CB099, CB153 and CB118) showed considerable decreases, while others (e.g., CB026, CB025) showed increases in relative abundance.

The general changes observed as a result of the dechlorinations include a decrease in concentration of selected higher molecular weight (MW) congeners and an increase in the abundance of selected lower MW PCBs. Another change as a result of dechlorinations of PCBs in sediments from the SS is the degradation of mono ortho substituted congeners. Mono-ortho substituted congeners and coplanar (non-ortho) congeners induce mixed function oxidase enzyme systems and are considered toxic (Kannan et al., 1988). Examinations of dechlorinations of coplanar compounds (which are considered more toxic than mono-ortho substituted compounds) are underway. Preliminary results indicate that coplanar congeners are also broken down as a result of dechlorinations in the NBHSS. Changes in the PCB mixtures as a result of dechlorinations in the SS will result in a PCB residue which is lower in molecular weight (and therefore less persistent in the environment) and less toxic as measured by capability to induce MFO enzyme systems. It is emphasized, however, that a large quantity of partially dechlorinated PCBs remain in the sediments of the NBHSS and the toxicity of the remaining mixtures is not known.

Plots of the relative abundance of peaks CB025 (structure 24-3), CB105 (structure 34-234), CB118 (structure 34-245), and CB153 (structure 245-245) demonstrate the variability in dechlorination between locations, core sections and congeners (Figure 3a-d). These figures show the magnitude of increase or decrease in abundance of a peak measured in a sample relative to the predicted abundance of that peak in the mixture of A-1242 and A-1254 standards calculated as input for the sample.

The plot of the relative abundance of CB025 shows a decrease in the BRH sample, but increases of varying magnitude are observed in samples from the SS and lower NBH. The congener which comprises this peak (CB025) is a minor component of A-1242 and A-1254 and its increase in samples has been reported as indicative of a reductive dechlorination process (Brown et al., 1987b). Most of the samples from the SS show a factor of 4 or more increase in relative abundance of this congener. Core section I14 12-13 and all sections of core H22 show relative increases which are similar to those observed for lower NBH cores C6 and C7. Increases in relative abundance from the 0-1 and 2-3 inch sections to the 6-7 and 12-13 inch sections are found in cores I11, and H17, but differences are not pronounced within cores except for the I14 12-13 inch section. The lower relative abundances of CB025 in I14 12-13 and the H22 core may reflect conditions which are unfavorable to dechlorination or retard dechlorination rates. The increases in relative abundance observed in C6 and C7 cores may demonstrate the initiation of dechlorination in these samples or may reflect down bay transport and deposition of partially dechlorinated residues.

Plots of the relative abundance of peak CB105 shows only small changes for BRH, H22 2-3 and cores C6 and C7, however, samples from the SS show considerable decreases in abundance of this congener. Lowered relative abundance of CB105 also has been found to be indicative of dechlorination in sediments from the Hudson River (Brown et al., 1984). For cores I11, H17 and H22 considerable decreases in relative abundance of CB105 are observed between the top (0-1 and 2-3 inch) and lower (6-7, 12-13, 18-19) core sections. These findings show residues are more dechlorinated near the plant and at depth in core sections than in surface sections in lower NBH.

Plots of the relative abundance of CB118 showed BRH, H22, H26 and lower NBH (C6 and C7) samples had small increases, but other SS samples, except for I14 12-13, showed decreases. In the SS the greatest decreases are found in the 6-7 inch sections with upper core sections (0-1 and 2-3 inch sections) showing smaller losses. Core section I11 6-7 shows the greatest loss.

A relative abundance plot of CB153 shows an increase in this congener in all samples except for I1167, I1112-13 and I1118-19 (Figure 3d). The greatest relative decrease is observed for I1167.

Comparison of the relative abundance plots for these four compounds between the sediment samples shows that the dechlorination processes are not proceeding at equal rates or to equal extents. It appears from these data that the dechlorinations (which are presumably anaerobic microbial processes) may be a stepped series of dechlorinations with each change in step occurring when the concentration of substrate falls below a suitable level. For example, all sections of core I11 show considerable decreases in relative abundance of CB105, but the decreases are much smaller for the 0-1 and 2-3 inch sections for CB118. For CB153 only core section 6-7 shows large decreases in relative abundance. It appears that the dechlorinating organisms may have depleted the CB105 in section 6-7 then switched to CB118 and then to CB153. The dechlorinations in other samples are less advanced in the stepwise process. An alternative explanation for this switching is that different bacteria are responsible for the dechlorinations. In this hypothesis, as a substrate (e.g., CB105) is completely utilized by one bacterial strain another organism multiplies to utilize a different substrate (e.g., CB118). These processes also could cause the observed distributions.

The plots for CB105, CB118 and CB153 show the differences in the extent of dechlorination between congeners and sites and illuminate the difficulties in determining dechlorination rates. From these plots it is evident that to estimate rates of dechlorination the congeners being dechlorinated and the sample location must be specified. A further difficulty in estimating rates of dechlorination in the SS and NBH is that the history of PCB inputs to the SS have not been maintained in the sediments.

Although the Aroclor mixtures utilized and presumably discharged by the plant changed over the years of manufacture distinct changes in inputs are not reflected in samples from sediment cores. PCBs were used as impregnation fluids in capacitors from 1947 until 1978. Plant records show A-1254 was utilized until 1963 when it was replaced with A-1242. In 1971, A-1016 completely replaced A-1242 as an impregnation fluid

(Weaver, 1982).

Measurements and estimates of sediment depositional rates in NBH vary considerably depending on location and have increased substantially from a few mm/year to a few centimeters/year since construction of the Hurricane Barrier in 1966 (Summerhayes et al., 1977). A computer model of the SS utilized to predict the distribution and fate of PCBs utilizes a sediment deposition rate of < 1 mm/year (Dr. Gerald Miller, 1989, personal communication), while another report estimates the rate at approximately 3 mm/year (U.S. Army Corps of Engineers, 1988). Using these estimates of depositional rates, the depth in the sediment which corresponds to the change from A-1254 to A-1242 in 1963 would be (1989-1963 = 25 years) between 2.5 and 7.5 cm (about 1 to 3 inches). As described earlier, depths of the changes from A-1254 to A-1242 varied in the core samples taken in the SS (depth to change was > 19" in core H17), but depths to the change were all in excess of the 3 inches estimated from depositional rates. Further, sediment samples from the SS show mixtures of A-1242 and A-1254 in all sections suggesting that following input the different PCB mixtures were down mixed into sediments by benthic processes (e.g., bioturbation) or that mixtures percolated through sediments after deposition. Regardless of what process is responsible, it appears that the age of a contaminant in a sediment section within the SS may not be reliably estimated by using sediment depositional rates.

Although sediment deposition rates cannot be used to age PCB residues in cores from the SS, estimates of the average rates of dechlorination from input to time of sampling can be made by assuming the time of input of the Aroclor mixtures. Assuming an input of PCBs in 1963 and first order kinetics, rate constants and half lives were calculated for congeners CB031, CB105, CB118 and CB153 using sediment samples which are representative of lower (H2267) and higher (I1167) extents of dechlorination (Table 4). For CB031, the rate constants are .001 ($t^{-1}$) and .053 ($t^{-1}$) and the half lives are 465 years and 13.2 years for H2267 and I1167 samples, respectively. Considerable differences in half lives were also observed between congeners within the same sample. For example, sample H2267 has a half life of 465 years for CB031 and a half life of 7.5 years for CB105. These differences emphasize that estimates of dechlorination rates vary greatly depending on the congener and the sample. The calculated rate constants represent averages over the 25 year time period from input to sample collection; other average rate constants and half lives would be obtained if different input times were specified. The average rate constants do not give specific information regarding the past dechlorination rates. For example, the PCB congeners may have been dechlorinated over a short period of time followed by years of dormancy. Further, these average rate constants offer no information on present dechlorination rates (if any) or if and at what rate these processes will continue in the future.

## Conclusions

1. PCBs in sediments from the New Bedford Harbor Superfund Site (NBHSS) showed considerable compositional alterations relative to predicted starting mixtures of Aroclors 1242 and 1254. These alterations included (1) a relative loss of lower MW PCB congeners in all samples presumably due to dissolution and evaporation prior to incorporation into sediment, and (2) relative decreases in the content of specific PCB congeners and the build up of other congeners in some samples by processes which were presumed to be dechlorinations.

2. The dechlorination processes varied in extent between samples with the largest changes observed for samples closest to the outfall from the capacitor plant at the 6-7" sediment depth. There was a trend toward less dechlorinated residues with distance from the capacitor plant. Samples from lower NBH showed only small evidence of dechlorination while control samples from Black Rock Harbor, CT, showed none.

3. Samples with a lower extent of dechlorination showed relative decreases in abundance of specific congeners (e.g., P058, CB085, CB132, CB105). In more extensively dechlorinated samples relative decreases in abundance of these and other congeners (e.g., CB031, P045, P046, P047, P048, P053, CB099, CB153 and CB118), and increases in abundance of congeners (e.g., CB026, CB025) which resulted from loss of chlorine atoms from more highly chlorinated congeners were observed.

The potentially toxic coplanar and mono-ortho congeners appear to be among those congeners most readily dechlorinated in the NBHSS. Therefore, the dechlorination processes in the NBHSS may have decreased the potential toxicity (as measured by mixed function oxidase enzyme induction) of the PCB residues. However, large quantities of partially dechlorinated PCBs remain in the sediments of the NBHSS and the toxicities of these remaining mixtures are not known.

4. Considerable differences were observed in the calculated average rate constants for the dechlorinations depending on the sample and the congener.

Figure 1.

Map showing locations of cores taken in this study.

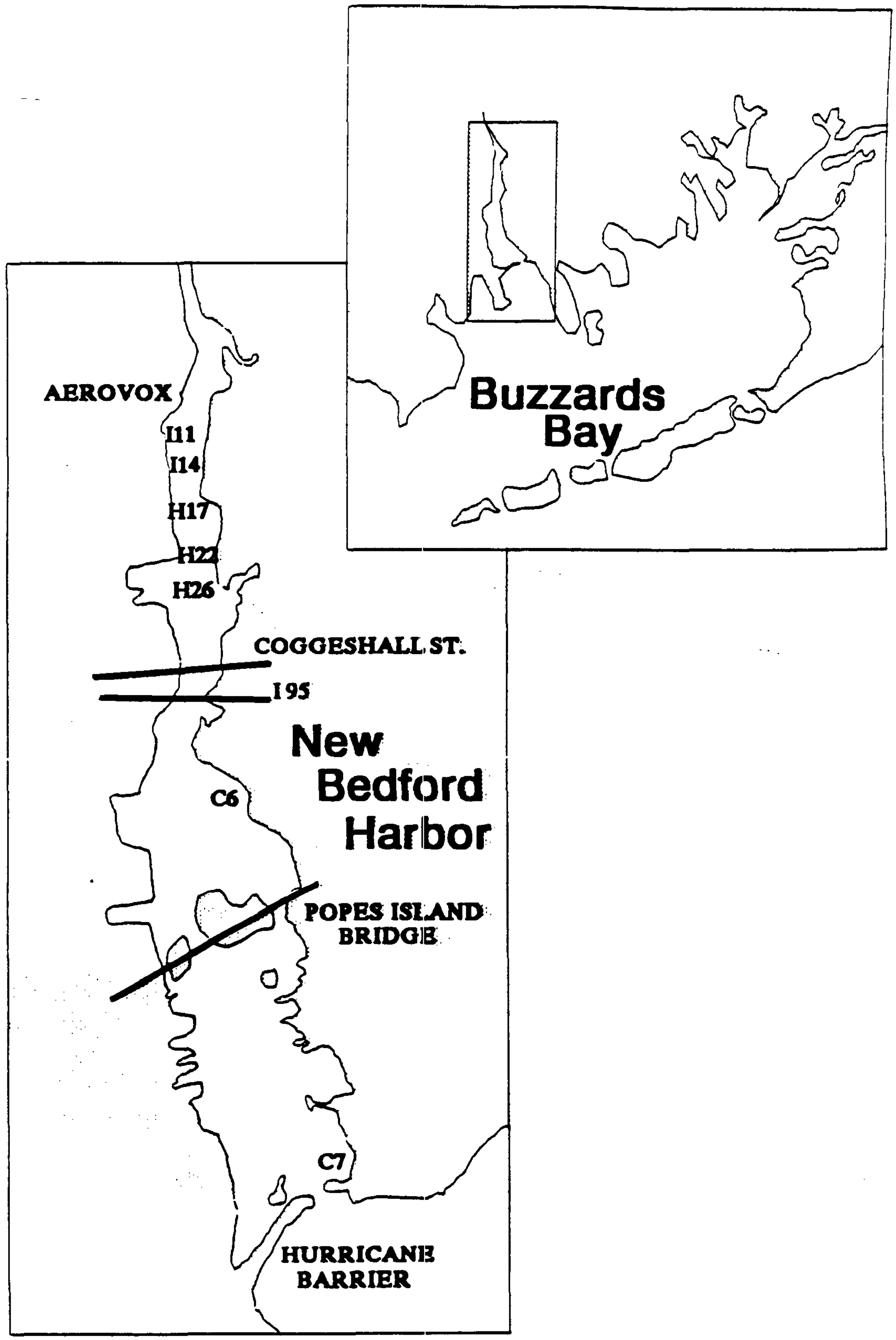

Buzzards
Bay
AEROVOX
I11
I14
H17
H22
H26
COGGESHALL ST.
I 95
New
Bedford
Harbor
C6
POPES ISLAND
BRIDGE
C7
HURRICANE
BARRIER

Figure 2.

(a) Comparative abundance plot for a 53%:47% (weight:weight) mixture of A-1242 and A-1254 standards.

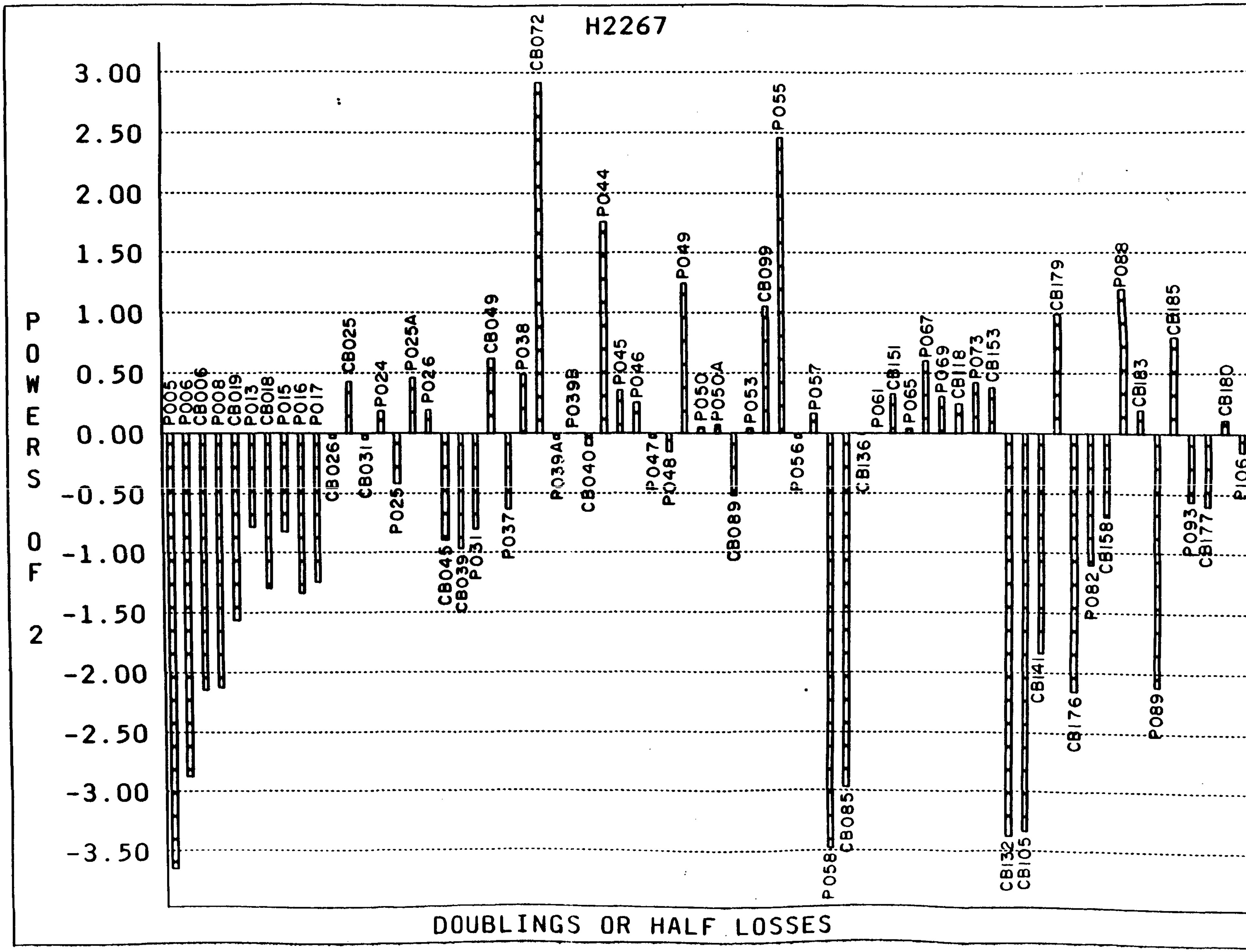
(b) Comparative abundance plot for six to seven inch section of core H22 (H2267).

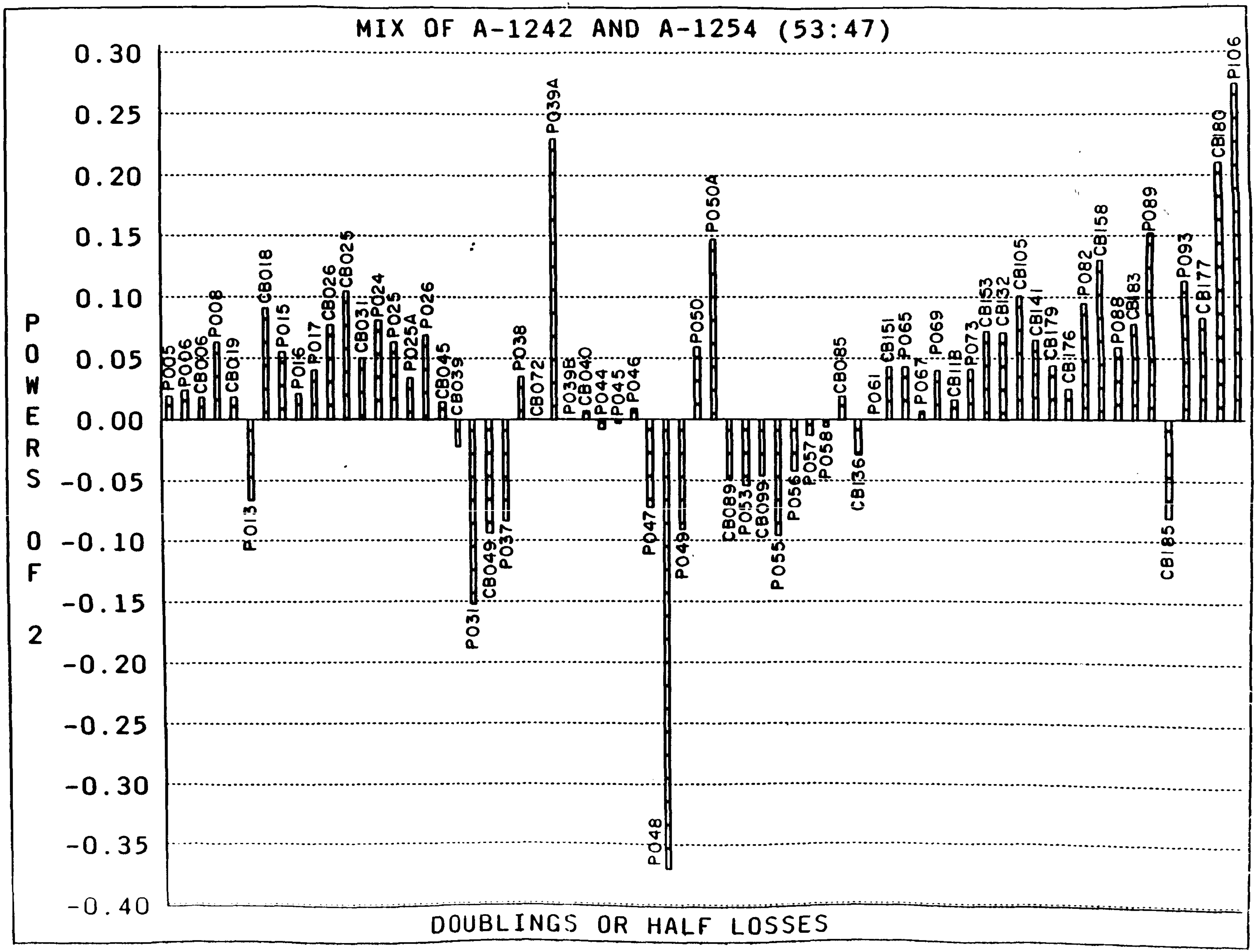
(c) Comparative abundance plot for six to seven inch section of core I11 (I1167).

(d) Comparative abundance plot for Black Rock Harbor sediment.

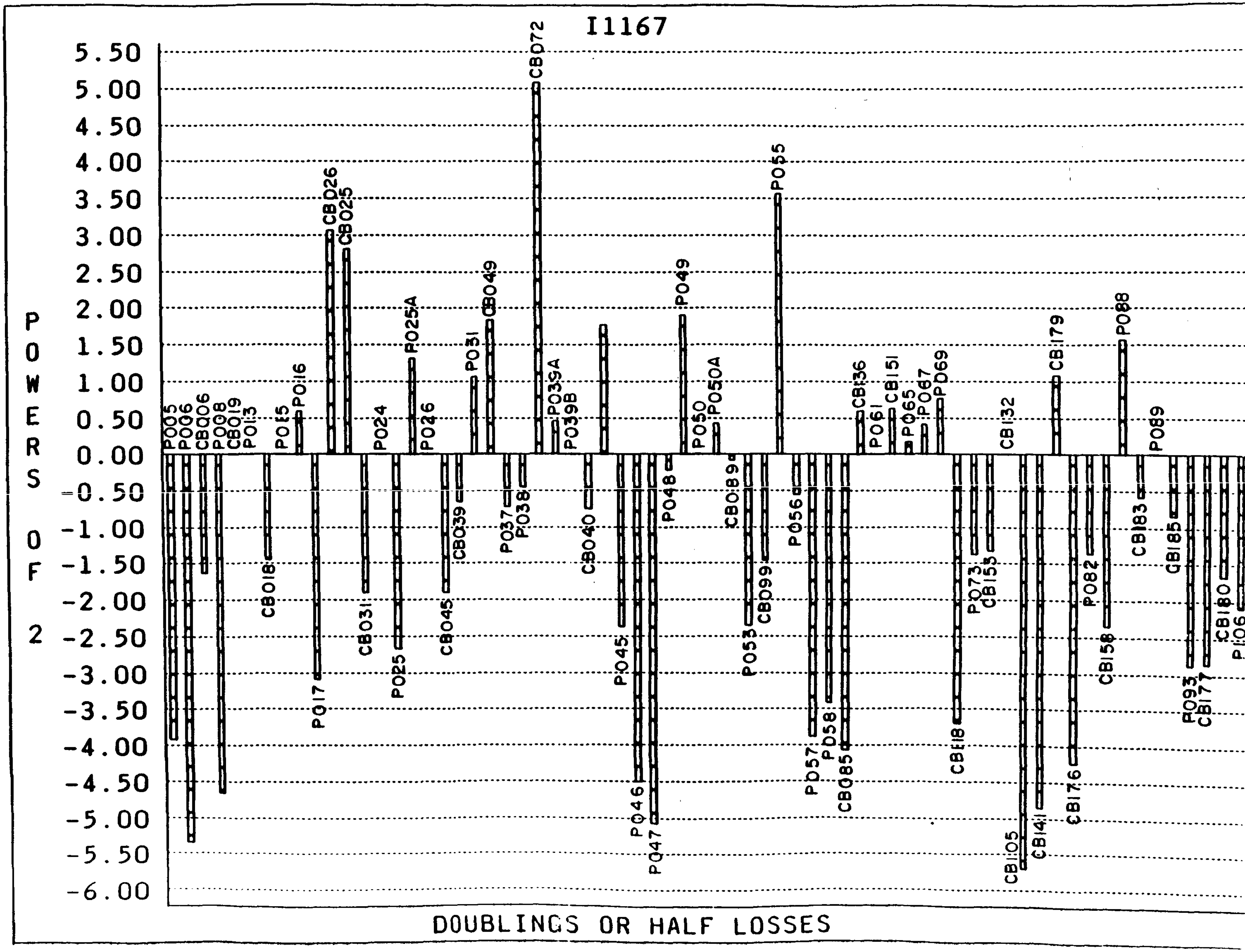
(e) Comparative abundance plot for six to seven inch section of core C7 (C767).

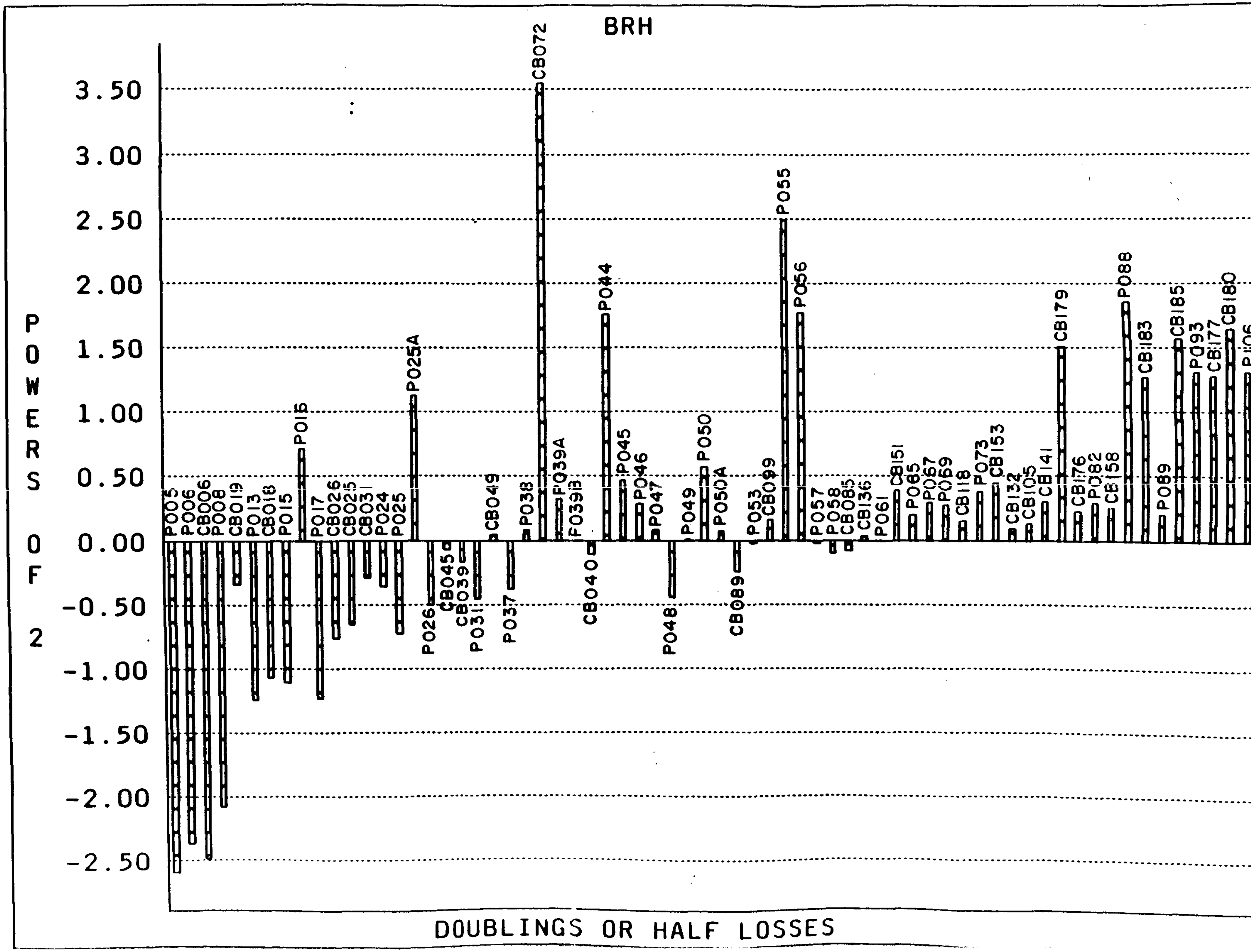
Plots were made by determining the original mix of PCBs using peaks P039B and P061 which are representative of A-1242 and A-1254 inputs, respectively, but appear to be resistant to reductive dechlorinations. Measured abundances relative to the predicted starting mix of A-1242 and A-1254 are shown by the length of bars and is expressed to the power of two. Therefore, a value of 2 would indicate the measured abundance of that peak in the sediment was 4 times above the computer prediction of the abundance of that peak in the A-1242 and A-1254 inputs which were incorporated in the sediment. A value of -2 shows that the abundance of that peak is 1/4 of the computer prediction of the original input.


H2267
POWERS OF 2
DOUBLINGS OR HALF LOSSES
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50



MIX OF A-1242 AND A-1254 (53:47)
POWERS OF 2
DOUBLINGS OR HALF LOSSES
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40


I1167
POWERS OF 2
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
-3.00
-3.50
-4.00
-4.50
-5.00
-5.50
-6.00
DOUBLINGS OR HALF LOSSES
P005
P006
CB006
P008
CB019
P013
CB018
P015
P016
P017
CB026
CB025
CB031
P024
P025
P025A
P026
CB045
CB039
P031
CB049
P037
P038
CB072
P039A
P039B
CB040
P045
P046
P047
P048
P049
P050
P050A
CB089
P053
CB099
P055
P056
P057
P058
CB085
CB136
P061
CB151
P065
P067
P069
CB118
P073
CB153
CB132
CB105
CB141
CB179
CB176
P082
CB158
P088
CB183
P089
CB185
P093
CB177
CB180
P106


BRH
POWERS OF 2
DOUBLINGS OR HALF LOSSES
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
P005
P006
CB006
P008
CB019
P013
CB018
P015
P016
P017
CB026
CB025
CB031
P024
P025
P025A
P026
CB045
CB039
P031
CB049
P037
P038
CB072
P039A
P039B
CB040
P044
P045
P046
P047
P048
P049
P050
P050A
CB089
P053
CB099
P055
P056
P057
P058
CB085
CB136
P061
CB151
P065
P067
P069
CB118
P073
CB153
CB132
CB105
CB141
CB179
CB176
P082
CB158
P088
CB183
P089
CB185
P093
CB177
CB180
P106

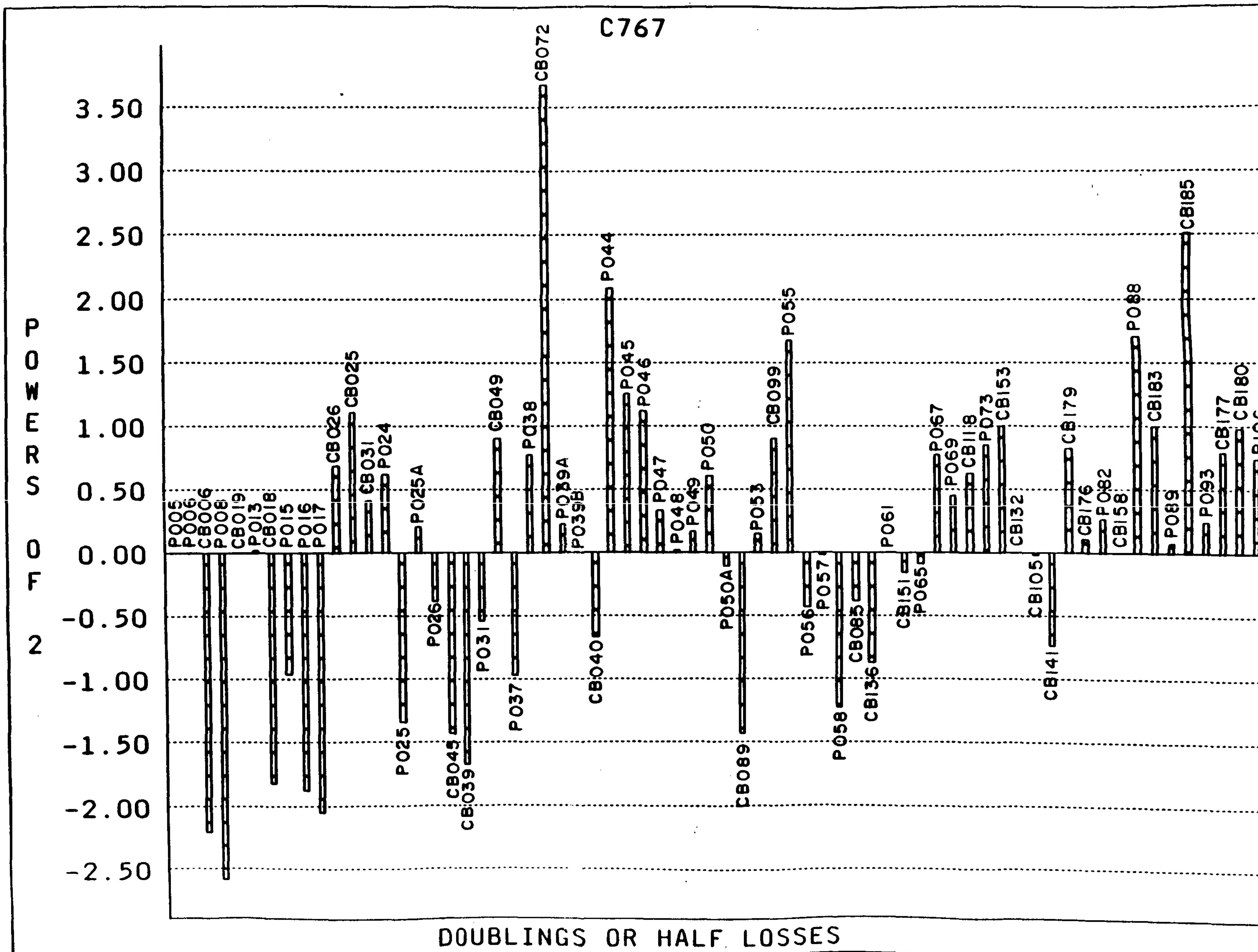
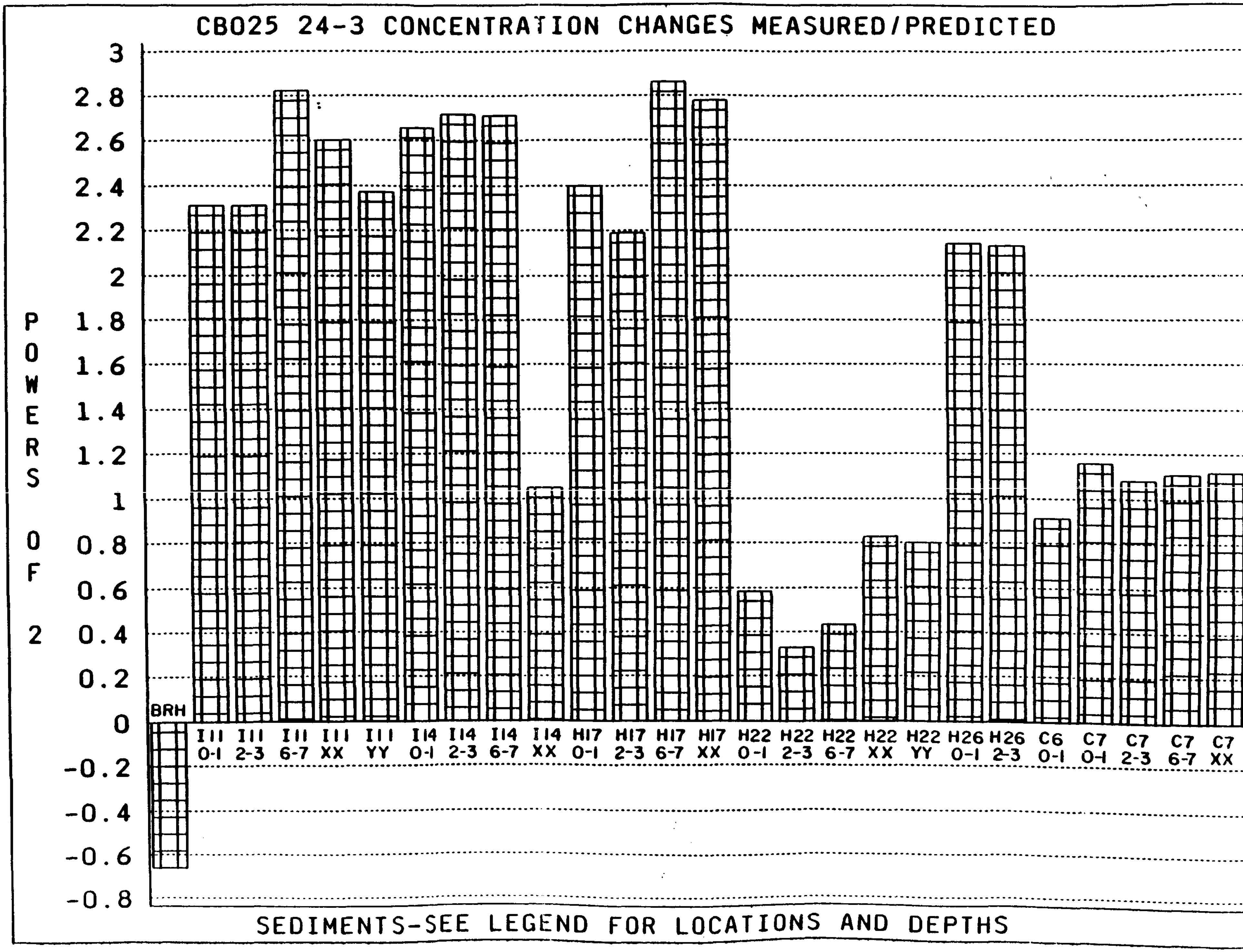
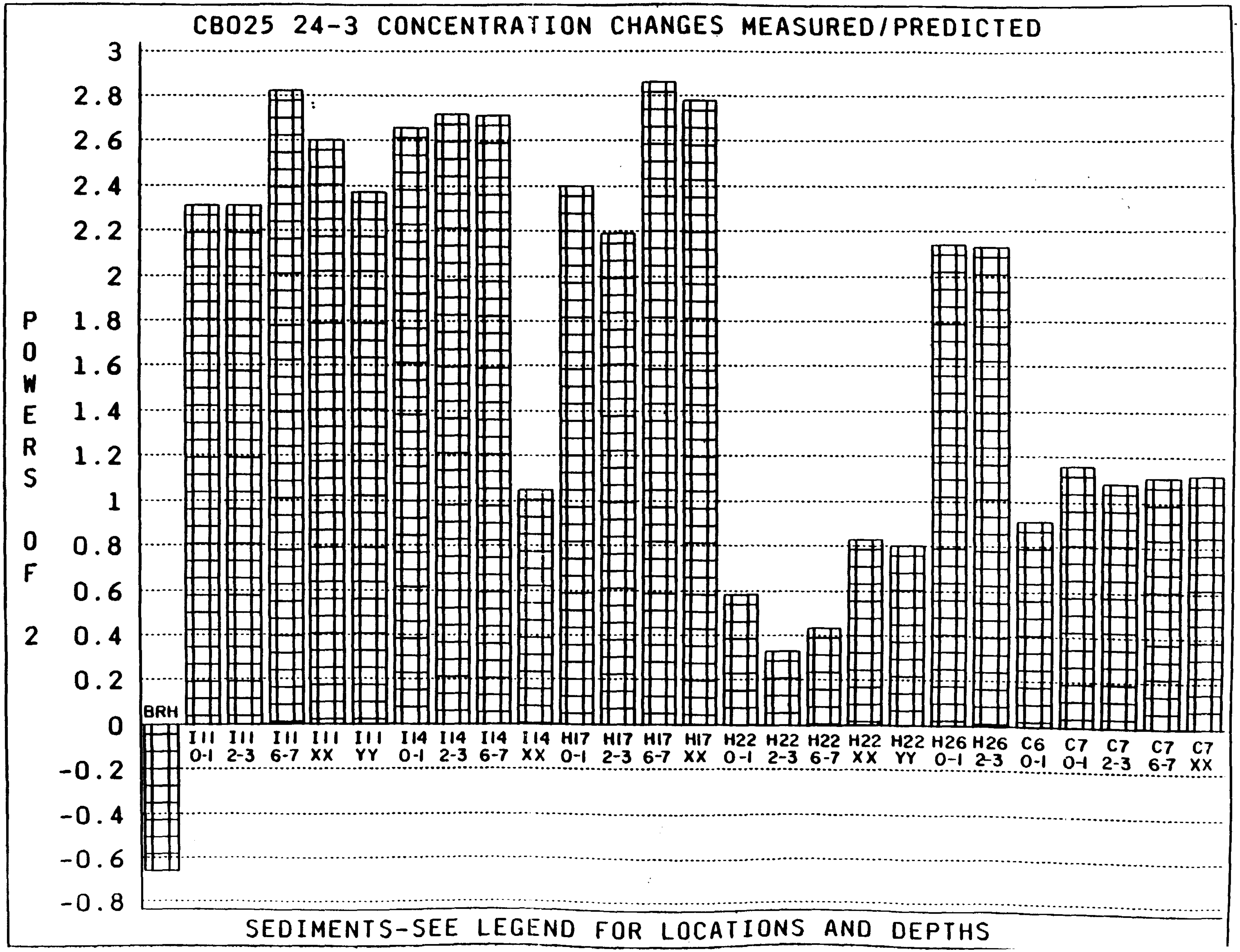

C767
POWERS OF 2
DOUBLINGS OR HALF LOSSES
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
-2.50
CB072
P044
CB185
P055
P088
CB025
P045
P046
CB049
CB099
CB153
CB179
CB183
CB180
P106
CB026
P024
CB031
P038
P050
P067
CB118
P073
P069
CB177
P025A
P039A
P039B
P047
P048
P049
P053
P061
CB132
CB176
P082
CB158
P089
P093
P005
P006
CB006
P008
CB019
P013
CB018
P015
P016
P017
P025
P026
CB045
CB039
P031
P037
CB040
P050A
CB089
P056
P057
P058
CB085
CB136
CB151
P065
CB105
CB141

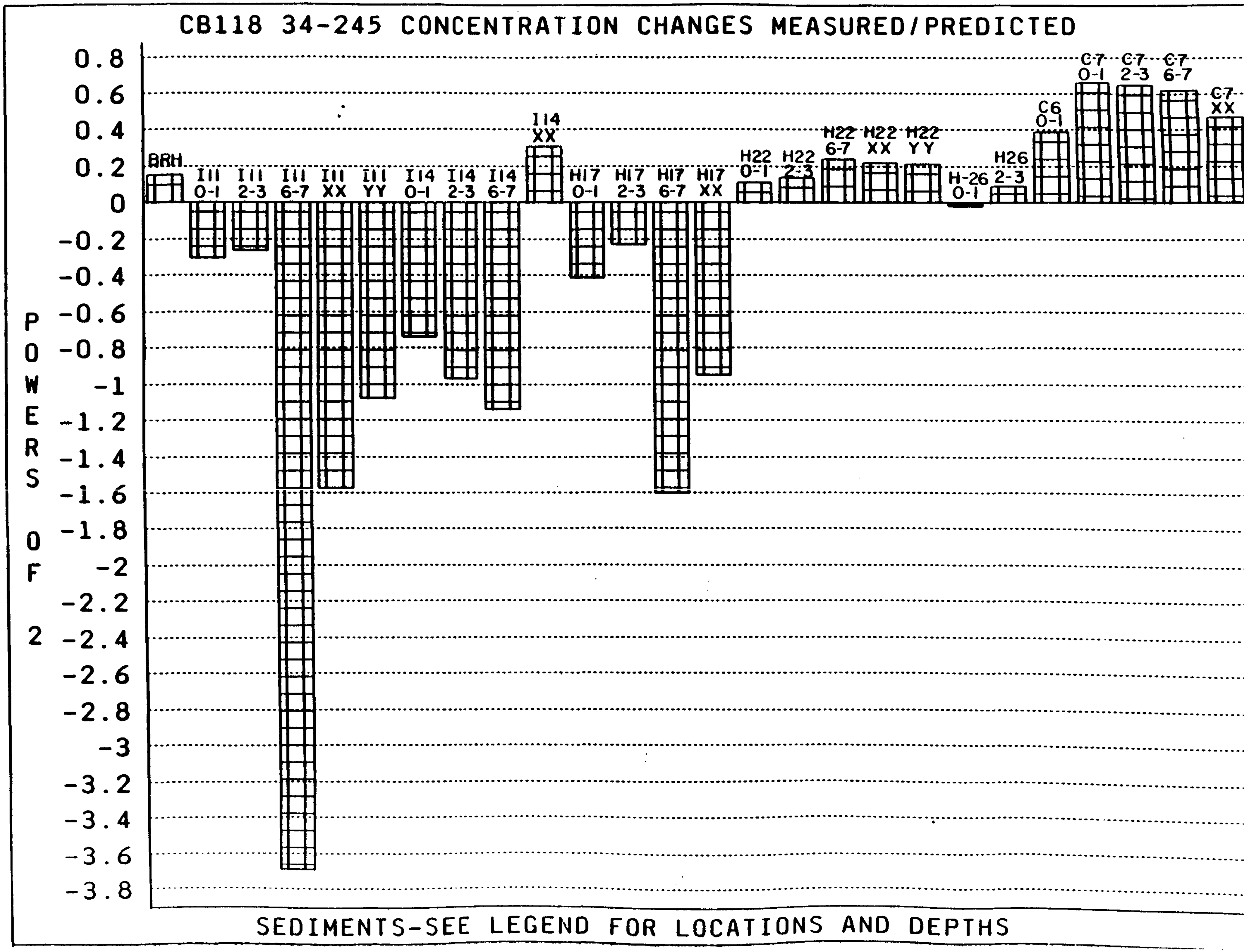
Figure 3.

Figure 3 a-d show the magnitude of increase or decrease in abundance of a peak measured in a sample relative to the predicted abundance of that peak in the mixture of A-1242 and A-1254 standards calculated as input for the sample. Peaks and structure of dominant congener comprising the peak are shown in label of Figure. Samples are identified as labels for bars and numbers indicate depth of core sections in inches. BRH sample is at extreme left in Figures. Cores are ordered (left to right) in increasing distance from the outfall of the capacitor plant (see Figure 1).


CB025 24-3 CONCENTRATION CHANGES MEASURED/PREDICTED
POWERS OF 2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
BRH
I11 0-1
I11 2-3
I11 6-7
I11 XX
I11 YY
I14 0-1
I14 2-3
I14 6-7
I14 XX
H17 0-1
H17 2-3
H17 6-7
H17 XX
H22 0-1
H22 2-3
H22 6-7
H22 XX
H22 YY
H26 0-1
H26 2-3
C6 0-1
C7 0-1
C7 2-3
C7 6-7
C7 XX
SEDIMENTS-SEE LEGEND FOR LOCATIONS AND DEPTHS



CB025 24-3 CONCENTRATION CHANGES MEASURED/PREDICTED
POWERS OF 2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
BRH
I11 0-1
I11 2-3
I11 6-7
I11 XX
I11 YY
I14 0-1
I14 2-3
I14 6-7
I14 XX
H17 0-1
H17 2-3
H17 6-7
H17 XX
H22 0-1
H22 2-3
H22 6-7
H22 XX
H22 YY
H26 0-1
H26 2-3
C6 0-1
C7 0-1
C7 2-3
C7 6-7
C7 XX
SEDIMENTS-SEE LEGEND FOR LOCATIONS AND DEPTHS


CB118 34-245 CONCENTRATION CHANGES MEASURED/PREDICTED
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
-2
-2.2
-2.4
-2.6
-2.8
-3
-3.2
-3.4
-3.6
-3.8
POWERS OF 2
BRH
I11 0-1
I11 2-3
I11 6-7
I11 XX
I11 YY
I14 0-1
I14 2-3
I14 6-7
I14 XX
H17 0-1
H17 2-3
H17 6-7
H17 XX
H22 0-1
H22 2-3
H22 6-7
H22 XX
H22 YY
H-26 0-1
H26 2-3
C6 0-1
C7 0-1
C7 2-3
C7 6-7
C7 XX
SEDIMENTS-SEE LEGEND FOR LOCATIONS AND DEPTHS

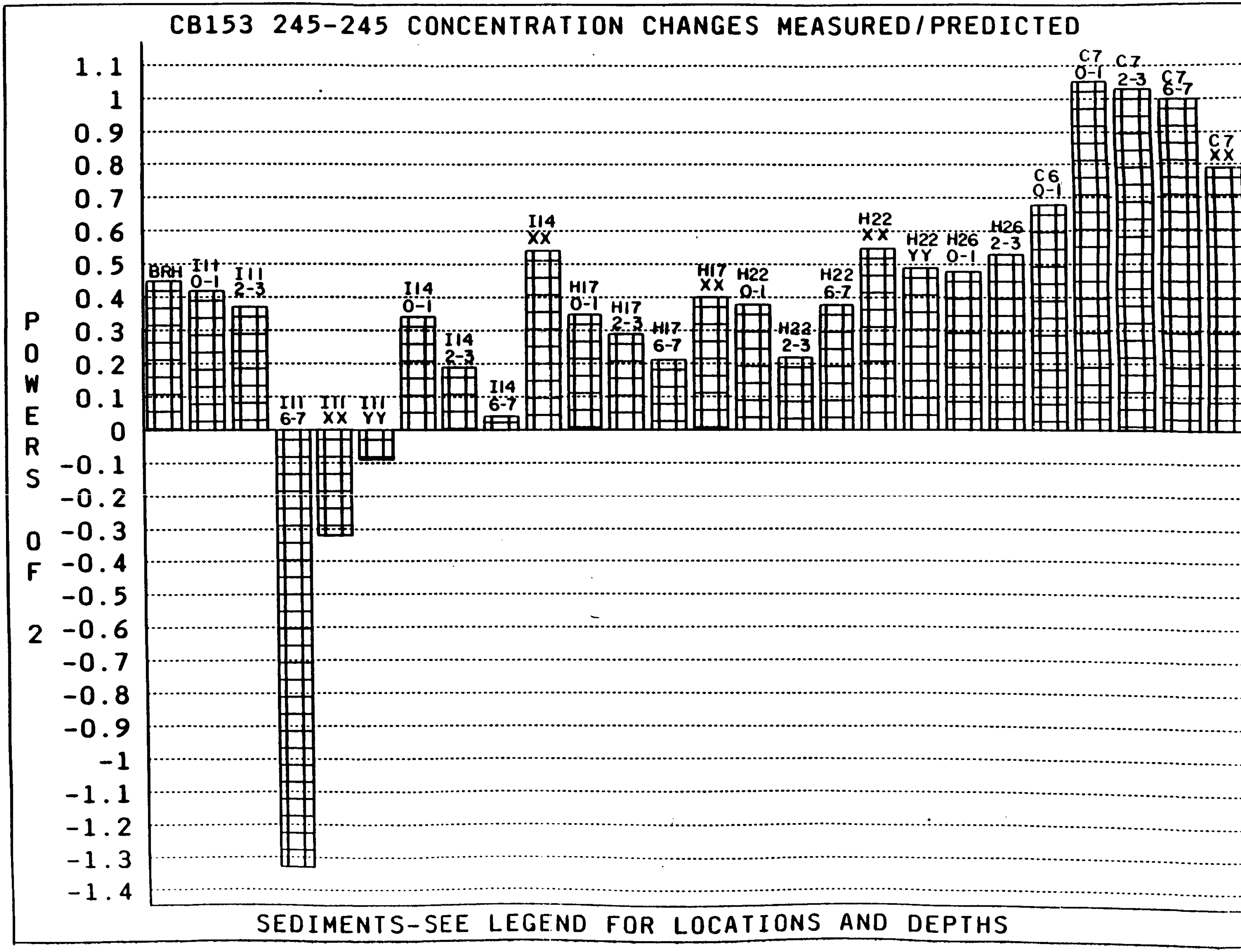

CB153 245-245 CONCENTRATION CHANGES MEASURED/PREDICTED
POWERS OF 2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
-1.3
-1.4
BRH
I11 0-1
I11 2-3
I11 6-7
I11 XX
I11 YY
I14 0-1
I14 2-3
I14 6-7
I14 XX
H17 0-1
H17 2-3
H17 6-7
H17 XX
H22 0-1
H22 2-3
H22 6-7
H22 XX
H22 YY
H26 0-1
H26 2-3
C6 0-1
C7 0-1
C7 2-3
C7 6-7
C7 XX
SEDIMENTS-SEE LEGEND FOR LOCATIONS AND DEPTHS

Table 1.

Locations and Lengths of Cores Collected in New Bedford Harbor

| Core | Location (Loran) | Length (inches) |
|---|---|---|
| I-11 | 252293N<br>759132E | 37 |
| I-14 | 244549N<br>759153E | 42 |
| H-17 | 243785N<br>758908E | 38 |
| H-22 | 242558N<br>758887E | 48 |
| H-26 | 241555N<br>758917E | 30 |
| C-6 | 236700N<br>760200E | 31 |
| C-7 | 229730N<br>762900E | 22 |

Table 2

Peaks, Corresponding Congeners and Structures

| Peak ID[1] | Tentative[2] Identification[3] of Congeners[4,5] | Structure[6] |
|---|---|---|
| P005 | 10(S),4(S) | 26-,2-2 |
| P006 | 7(S),9(S) | 24-,25- |
| CB006 | 6(S) | 2-3 |
| P008 | 5(S),8(S) | 23-,2-4 |
| CB019 | 19(L) | 2-26 |
| P013 | 12(S),13(S) | 34-,3-4 |
| CB018 | 18(S) | 2-25 |
| P015 | 15(S),17(L) | 4-4,2-24 |
| P016 | 24(L),27(L) | 236-,3-26 |
| P017 | 16(S),32(L) | 2-23,4-26 |
| CB026 | 26(S) | 25-3 |
| CB025 | 25(L) | 24-3 |
| CB031 | 31(S) | 25-4 |
| P024 | 28(S),50(S)(M) | 24-4,2-246 |
| P025 | 20(S),21(S)(M),53(S),33(S) | 23-3,234-,25-26,2-34 |
| P025A | No I.D. | |
| P026 | 22(L),51(L) | 23-4,24-26 |
| CB045 | 45(L) | 2-236 |
| CB039 | 39(L)(M) | 35-4 |
| P031 | 52(S),73(L)(M) | 25-25,26-35 |
| CB049 | 49(S) | 24-25 |

---

1 Peak designation as P numbers are used for peaks containing coeluting congeners or where identifications are ambiguous.

2 Identifications listed as tentative because standards for all congeners were not available and other congeners may coelute in the peaks listed.

3 (S) identified by coinjection of standard; (L) identified by comparison with literature values (Brown and Wagner, 1986; Schulz et al., 1989).

4 Numbering according to Ballschmiter and Zell (1980).

5 Dominant congeners (believed to comprise $\geq$ 90% of peaks) are underlined. Congeners comprising < 0.5% of Aroclors are identified by (M) (Schultz et al., 1989).

6 Numbers indicate position of chlorine atoms on each ring.

Table 2 (cont.)

| | | |
|---|---|---|
| P037 | 44(S),104(S)(M) | 23-25,26-246 |
| P038 | 37(S),42(S),59(L) | 3-34,23-24,3-236 |
| CB072 | 72(S)(M) | 25-35 |
| P039A | No I.D. | |
| P039B | 71(L)(M),64(L), | 26-34,4-236,2-234 |
| CB040 | 40(S) | 23-23 |
| P044 | 100(S),67(L) | 24-246,25-34 |
| P045 | 58(L)(M),63(L) | 23-35,4-235 |
| P046 | 74(L),94(L)(M) | 4-245,26-235 |
| P047 | 70(S),61(S)(M),76(L) | 25-34,2345-,2-345 |
| P048 | 66(S),93(S)(M),95(L) | 24-34,2-2356,25-236 |
| P049 | 91(L),98(L)(M),55(L)(M) | 24-236,23-246,3-234 |
| P050 | 56(L) | 23-34 |
| P050A | 60(S) | 4-234 |
| CB089 | 89(L)(M)(+ others 92,84) | 26-234 |
| P053 | 101(S),90(L) | 25-245,24-235 |
| CB099 | 99(L) | 24-245 |
| P055 | 150(L)(M),112(S)(M),119(S) | 236-246,3-2356,34-246 |
| P056 | 83(L),109(L)(M) | 23-235,3-2346 |
| P057 | 152(L)(M),97(S),86(S)(M) | 26-2356,23-245,2-2345 |
| P058 | 87(S),111(L)(M),115(S),81(S)(M) | 25-234,35-235,4-2346,4-345 |
| CB085 | 85(L) | 24-234 |
| CB136 | 136(S) | 236-236 |
| P061 | 77(S),110(S) | 34-34,34-236 |
| P064 | 151(S),82(L) | 25-2356,23-234 |
| P065 | 135(L),124(L)(M),144(L)(M) | 235-236,24-345,25-2346 |

Table 2 (cont.)

| | | |
|---|---|---|
| P067 | 107(L),108(L)(M),147(L)(M) | 34-235,35-234,24-2356 |
| P069 | 149(L),106(L)(M),123(L) | 245-236,3-2345,24-345 |
| CB118 | 118(S) | 34-245 |
| P073 | 146(L),161(L)(M) | 235-245,35-2346 |
| CB153 | 153(S) | 245-245 |
| CB132 | 132(L) | 234-236 |
| CB105 | 105(S) | 34-234 |
| CB141 | 141(S) | 25-2345 |
| CB179 | 179(L) | 236-2356 |
| CB176 | 176(L) | 236-2346 |
| P082 | 138(S),163(L)(M) | 234-245,34-2356 |
| CB158 | 158(S) | 34-2346 |
| P088 | 187(S),182(S)(M),159(S)(M) | 245-2356,246-2345,35-2345 |
| CB183 | 183(S) | 245-2346 |
| P089 | 128(S),167(L) | 234-234,245-345 |
| CB185 | 185(S) | 25-23456 |
| PO93 | 174(L),181(S)(M) | 236-2345,24-23456 |
| CB177 | 177(L) | 234-2356 |
| CB180 | 180(S) | 245-2345 |
| P106 | 170(S),190(L) | 234-2345,34-23456 |

Table 3

Concentrations and Percentages of Aroclor Mixtures in Sediments

| Sample | UGA1242+A1254/G(dry) | %A1242 | %A1254 |
|---|---|---|---|
| BRH | 21.4 | 42 | 58 |
| I1101 | 912 | 69 | 32 |
| I1123 | 2280 | 71 | 29 |
| I1167 | 2960 | 56 | 44 |
| I11XX | 12 | 63 | 37 |
| I11YY | 3.2 | 68 | 32 |
| I11ZZ | 0.5 | 61 | 39 |
| I1401 | 740 | 72 | 28 |
| I1423 | 1200 | 75 | 26 |
| I1467 | 1720 | 76 | 24 |
| I14XX | 161 | 52 | 48 |
| I14YY | 0.2 | 61 | 39 |
| H1701 | 507 | 71 | 29 |
| H1723 | 660 | 73 | 27 |
| H1767 | 1560 | 75 | 25 |
| H17XX | 16.6 | 71 | 29 |
| H17YY | 0.3 | 69 | 31 |
| H2201 | 414 | 75 | 25 |
| H2223 | 790 | 76 | 24 |
| H2267 | 753 | 50 | 50 |
| H22XX | 5.7 | 56 | 44 |
| H22YY | 1 | 56 | 44 |
| H2601 | 102 | 61 | 39 |
| H2623 | 10 | 54 | 46 |
| C601 | 2.1 | 39 | 61 |
| C701 | 9.4 | 36 | 64 |
| C723 | 7.4 | 37 | 63 |
| C767 | 7.6 | 39 | 61 |
| C7XX | 7.6 | 51 | 49 |

BRH = SEDIMENT FROM BLACK ROCK HARBOR CT.
OTHER NAMES REFER TO LOCATIONS IN NEW BEDFORD - SEE MAP FOR LOCATIONS.
XX = 12-13 INCH SECTION.
YY = 18-19 INCH SECTION.
ZZ = 24-25 INCH SECTION.

Table 4

Rate Constants and Half Lives for Dechlorination

of Selected PCB Congeners

| Congener | Rate Constants($t^{-1}$) | | Half Lives (years) | |
|---|---|---|---|---|
| | H2267 | I1167 | H2267 | I1167 |
| CB031 | .001 | .053 | 465 | 13.2 |
| CB105 | .092 | .16 | 7.5 | 4.4 |
| CB118 | *[1] | .10 | *[1] | 6.8 |
| CB153 | *[1] | .04 | *[1] | 18.8 |

[1] Peak showed increase in relative abundance therefore calculation of rate and half life were not made.

## References


Ballschmiter, K. and M. Zell. 1980. Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography:Composition of Technical Aroclor-and Clophen-PCB Mixtures. Fresenius Zeitschrift für Analytische Chemie, Vol 302:210-31.

Brown, J.F., D.L. Bedard, M.J., Brennan, J.C., Carnaham, H., Feng and R.E. Wagner. 1987(a). "Polychlorinated Biphenyl Dechlorinations in Aquatic Sediments." Science Vol 236:709-712.

Brown, J.F., Jr., R.E. Wagner, D.L. Bedard, M.J. Brennan, J.C. Carnaham, R.J. May and T.J. Tofflemire. 1984. PCB transformations in upper Hudson sediments. Northeast Environ. Sci. 3:167-179.

Brown, J.F., Jr., R.E. Wagner, H. Feng, D.L. Bedard, M.J. Brennan, J.C. Carnahan, and R.J. May. 1987(b). Environmental Dechlorination of PCBs. Environ. Tox. and Chem. Vol 6:579-593.

Brown, J.F., Jr., and R.E. Wagner. 1986. Polychlorinated Biphenyl (PCB) Movement and Transformation in Acushnet Estuary Sediments. Draft of September 26, 1988.

Kannan, N., S. Tanabe and R. Tatsukawa. 1988. Toxic Potential of Non-ortho and Mono-ortho Coplanar PCBs in Commercial PCB Preparations: "2,3,7,8-$T_4$ CDD Toxicity Equivalence Factors Approach." Bull. Environ. Contam. Toxicol. Vol 41:267-276.

Lake, J., G. Hoffman and S. Schimmel. 1985. "Bioaccumulation of Contaminants from Black Rock Harbor Dredged Material by Mussels and Polychaetes," Technical Report D-85-2, prepared by the U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, RI, for the U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Miller, Gerald, Ph.D. 1989. Personal Communication. Battelle. Duxbury, MA.

Plant Records. 1985. New Bedford harbor/Monsanto Total PCB by Each Customer for Each Year 11/22/1985, Customer Name: Aerovox.

Schulz, D.E., G. Petrick and J.C. Duinker. 1989. Complete characterization of Polychlorinated Biphenyl Congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional Gas Chromatography-Electron Capture Detection. Environ. Sci. Technol., Vol 23:852-859.

Summerhayes, C.P., J.P. Ellis, P. Stoffers, S.R. Briggs and M.G. Fitzgerald. 1977. Fine-Grained Sediment and Industrial Waste Distribution and Disposal in New Bedford Harbor and Western Buzzards Bay, Massachusetts, Woods Hold Oceanographic Institution. WHOI-76-115.

References (cont.)

U.S. Army Corps of Engineers. 1988. Technical Report EL-88-15. Dec. 88, Report #2.

Weaver, G. 1982. PCB Pollution in the New Bedford, Massachusetts, Massachusetts Coastal Zone Management, Commonwealth of Massachusetts.

## Appendix 1

### Residues in Organisms

The PCB patterns in extracts of organisms collected at the Southern end of the NBHSS (under the Coggeshall St. Bridge - see Figure 1) were compared with sediment extracts representative of low (sample H2267) and high (sample I1167) extents of dechlorination to determine the impact of dechlorination processes on the distributions of PCBs accumulated by these organisms. Te extracts from the fish (*Menidia menidia*) and oyster (*Crassostrea virginica*) were more similar to the extract from H2267, than to the extensively dechlorinated extract from I1167 (Figure A-1). The PCBs accumulated by the organisms, however, show even less dechlorination than the PCBs in sediment sample H2267. Decreases in the relative heights of peaks P058, CB085 and CB105, which appear to be sensitive indicators of dechlorination, are more pronounced in sediment H2267 than in the fish and oysters. Comparisons of gas chromatograms of organism extracts with different sediment extracts from the NBHSS showed the closest match between the organisms and H2201 (Figure A2). This surface sediment shows only minor dechlorination as indicated by the small relative decreases of peaks P058, CB085 and CB105 compared to the relative abundances of these peaks in a mixture of A-1242 and A-1254 standards (Figure A2). It appears that organisms exposed at the southern end of the NBHSS accumulated PCBs from sediments such as those at H2201 which showed only a minor extent of dechlorination. An alternative hypothesis that explains the patterns of these residues is that the organisms accumulated small amounts of heavily dechlorinated residues and large amounts of nondechlorinated residues.

## Analysis of Organism Samples

Mussels from each sample were homogenized using a polytron and 2 to 5 grams of each weighed into an acetone rinsed 100 ml centrifuge tube. Octachloronaphthalene was added as an internal standard. The samples were extracted with 25 ml of acetone by polytroning the sample and acetone in the centrifuge tube for 20 seconds. The sample was centrifuged and the supernatant poured into a 500 ml separatory funnel containing 150 ml of water. This procedure was repeated two more times combining extracts in the separatory funnel. The sample in the separatory funnel was then extracted three times with 25 ml portions of freon. The extracts were combined, treated with sodium sulfate and volume reduced using a heating mantle and a Kuderna-Danish evaporator with a 3-ball Snyder column. The extract was reduced in volume and solvent exchanged to about 10 ml of hexane. The sample was transferred to a concentrator tube and the volume adjusted to 10 ml. One ml was removed for lipid weight determination and the remaining 9 ml was partitioned against concentrated sulfuric acid. The sample was then volume reduced and solvent exchanged to 1 ml of heptane using a concentrator tube and stored in a screw-top vial prior to instrumental analysis. Extracts of organisms were analyzed using the same instrumental conditions used for the analysis of sediment samples.

## Appendix 2

### Recommendations for Future Work

In order to estimate the impact of dechlorination processes on the New Bedford Harbor Superfund Site (NBHSS) and on lower New Bedford Harbor and to allow better assessment of remediation options, the following areas of research should be addressed:

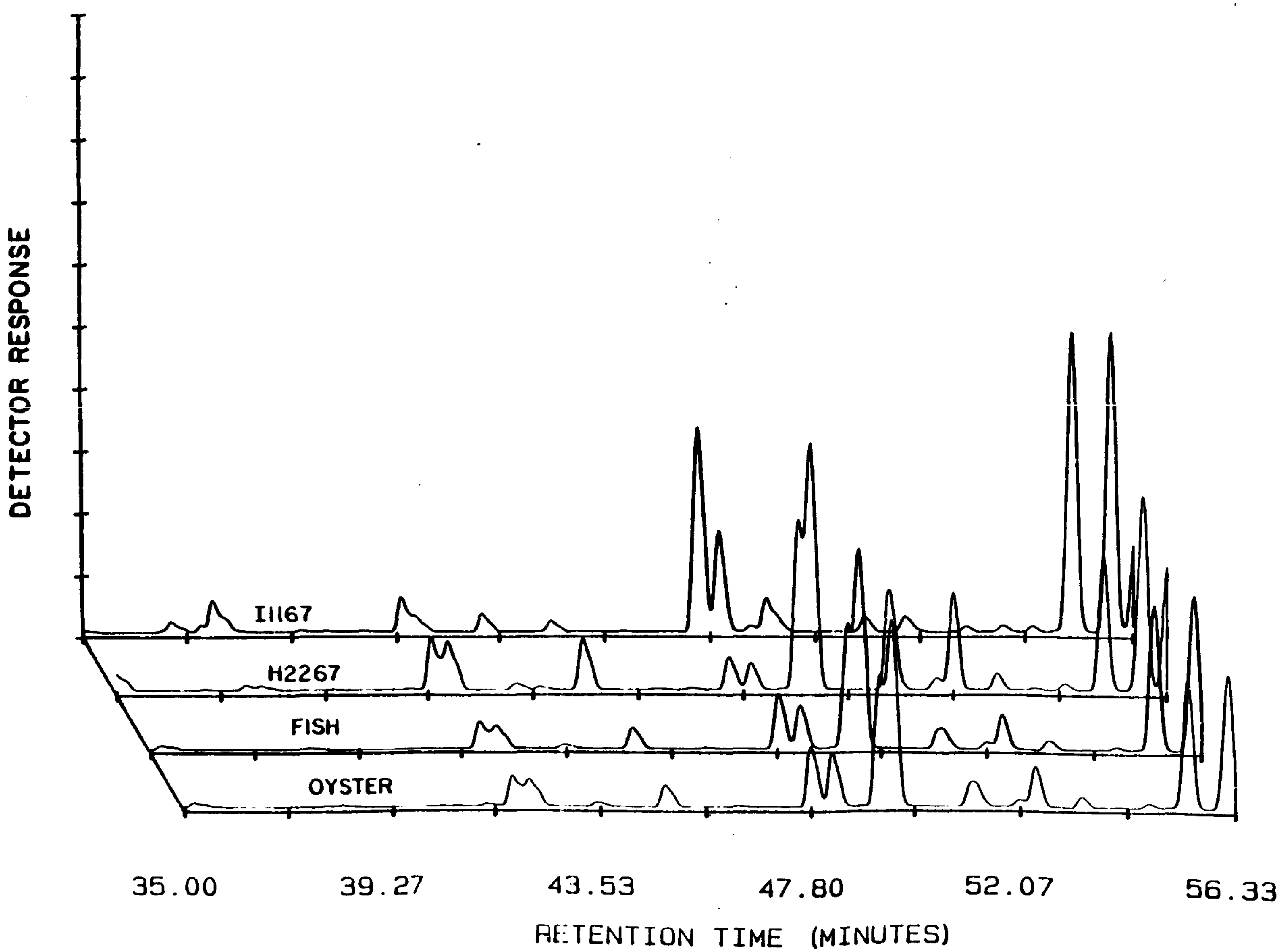
1. Determination of the extent of dechlorination of PCBs at the highest concentration locations in the NBHSS. The data in this report show that dechlorination processes are more extensive as the concentration of PCBs in sediments increases. In this study, however, the highest PCB concentrations in sediment were approximately 3 parts per thousand. At some locations near the outfall of the Aerovox plant the PCB concentrations are in excess of an order of magnitude higher than those reported in this study. Detailed analyses of the composition of PCBs present in sediments from these hotspot locations should be done to determine the extent of dechlorination which has occurred.

2. Studies should be conducted to determine the rates of dechlorination processes to allow predictions of the types and quantities of PCB which will be present in the future if no remediation of the NBHSS is undertaken.

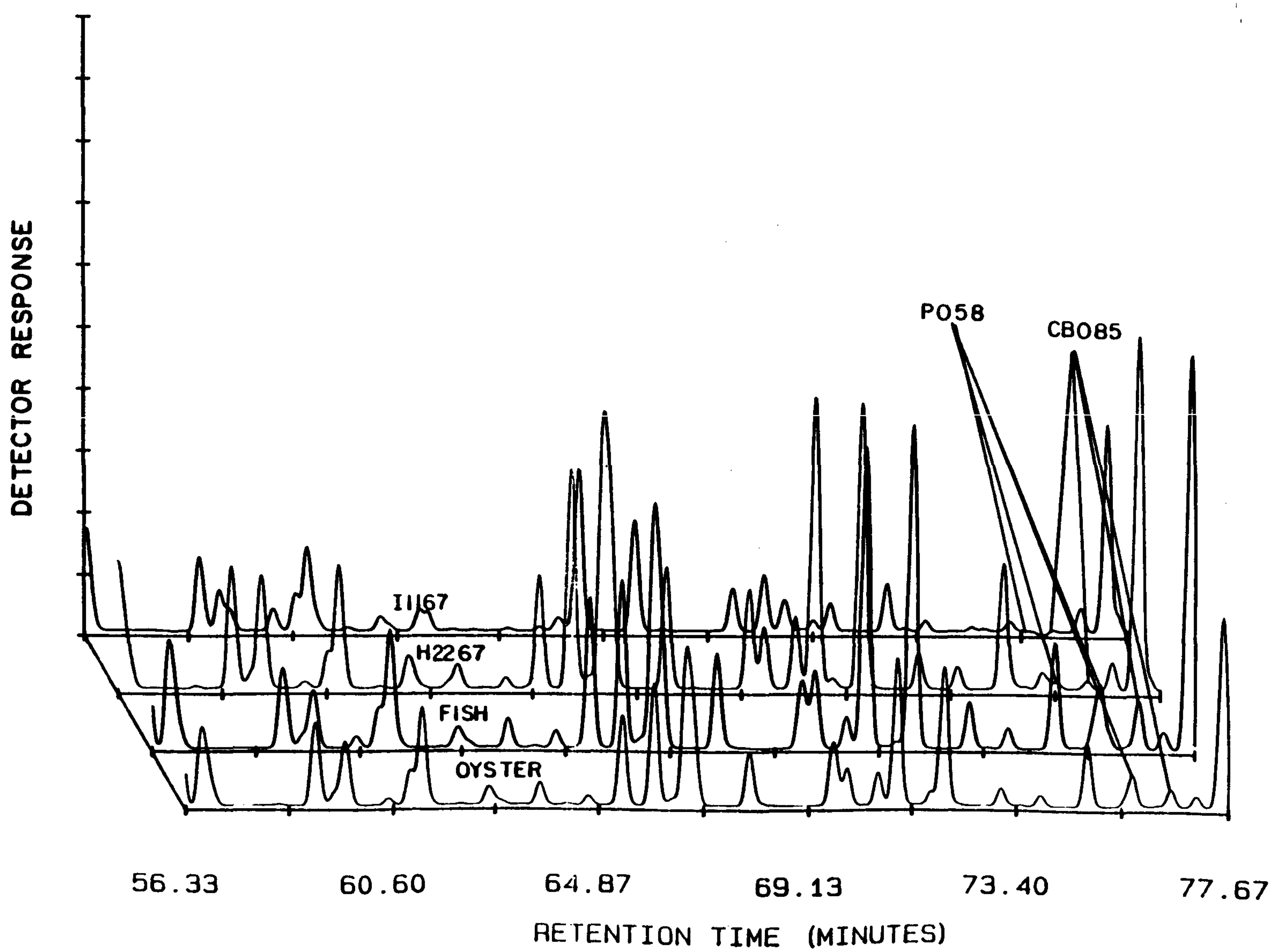
3. The toxicity of residues following dechlorination should be examined to allow evaluation of potential environmental benefits associated with these processes.

Figure A-1

Comparison of gas chromatograms from (top to bottom) sediment I1167, sediment H2267, fish (*Menidia menidia*) and oyster (*Crassostrea virginica*).



DETECTOR RESPONSE
I1167
H2267
FISH
OYSTER
35.00
39.27
43.53
47.80
52.07
56.33
RETENTION TIME (MINUTES)


DETECTOR RESPONSE
P058
CB085
I1167
H2267
FISH
OYSTER
56.33
60.60
64.87
69.13
73.40
77.67
RETENTION TIME (MINUTES)

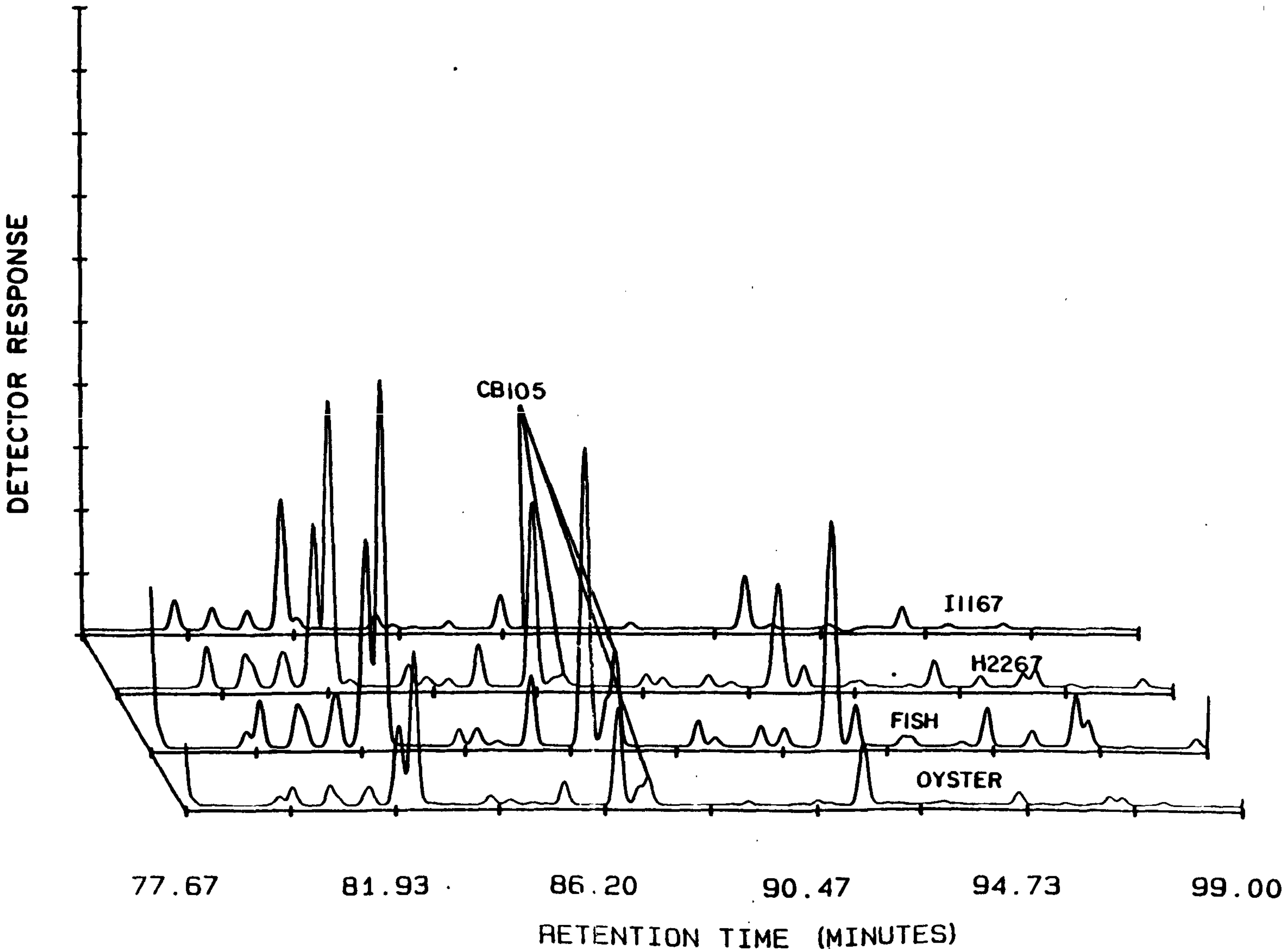
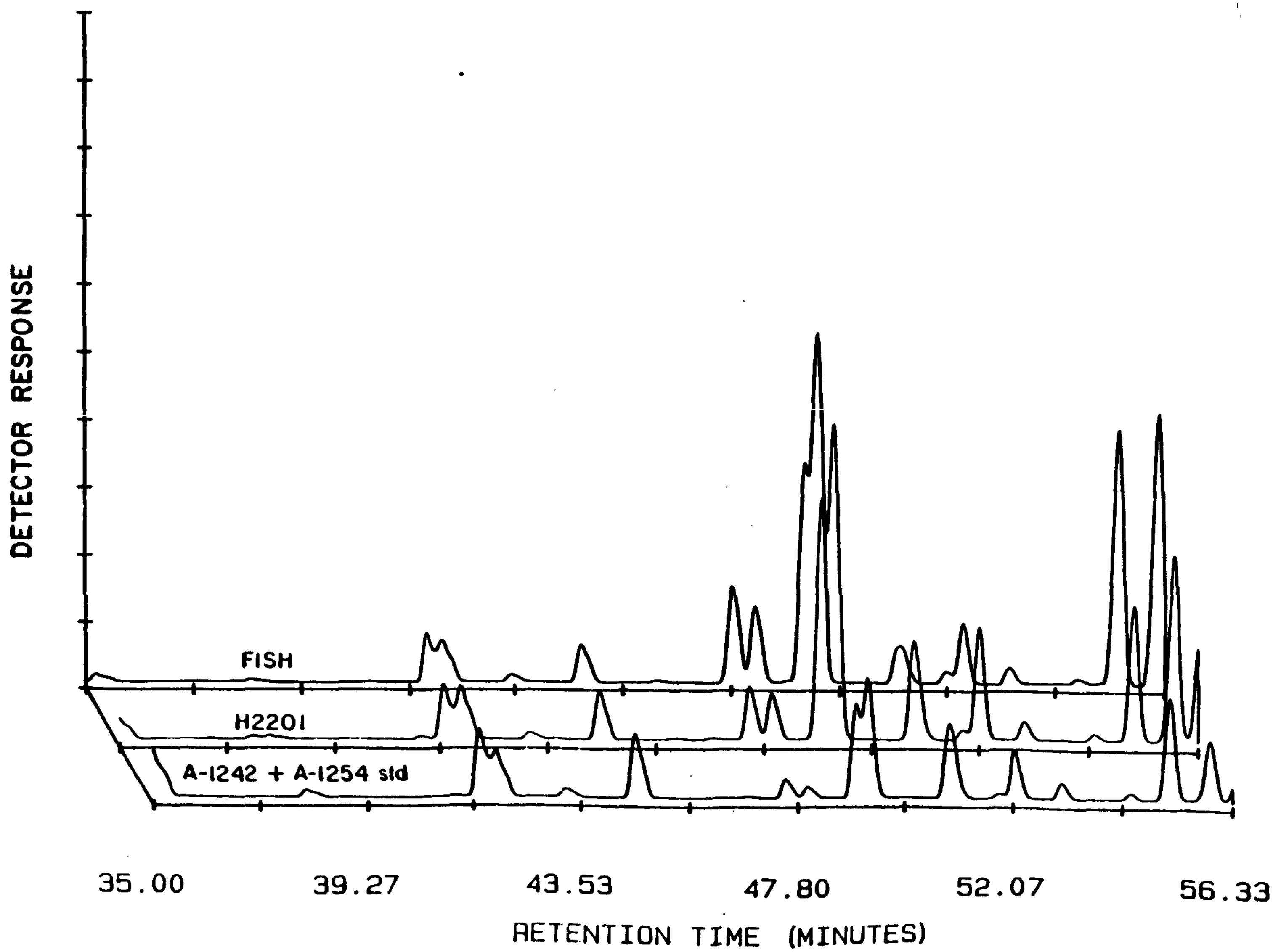
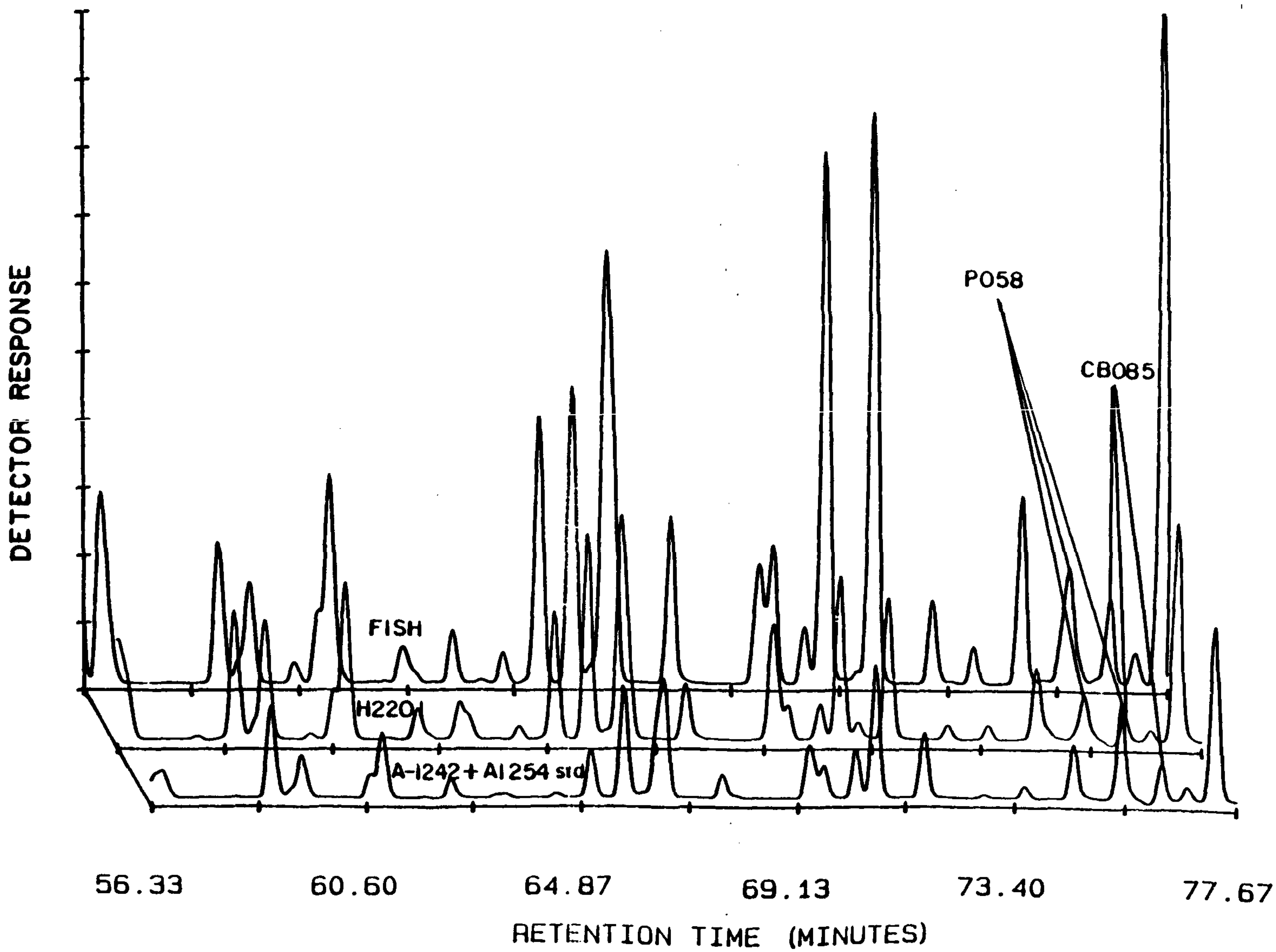

DETECTOR RESPONSE
CB105
I1167
H2267
FISH
OYSTER
77.67
81.93
86.20
90.47
94.73
99.00
RETENTION TIME (MINUTES)

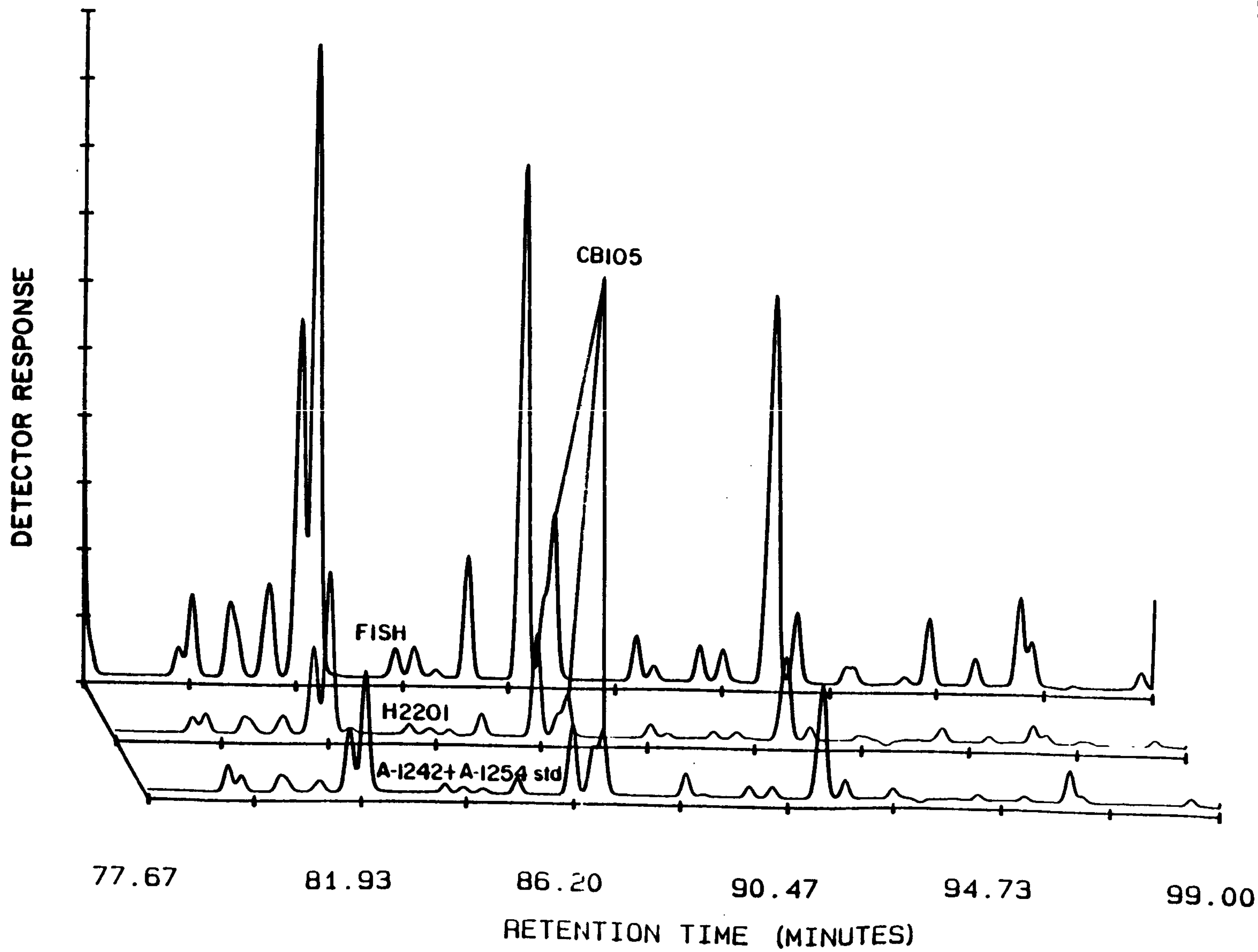
Figure A-2

Comparison of gas chromatograms from (top to bottom) fish (<u>Menidia menidia</u>), sediment H2201 and mixture of A-1242 and A-1254 standards (53:47% w/w).


DETECTOR RESPONSE
FISH
H2201
A-1242 + A-1254 std
35.00
39.27
43.53
47.80
52.07
56.33
RETENTION TIME (MINUTES)



DETECTOR RESPONSE
FISH
H220
A-1242+A1254 std
P058
CB085
56.33
60.60
64.87
69.13
73.40
77.67
RETENTION TIME (MINUTES)



DETECTOR RESPONSE
CB105
FISH
H2201
A-1242+A-1254 std
77.67
81.93
86.20
90.47
94.73
99.00
RETENTION TIME (MINUTES)

## Appendix 2

### Recommendations for Future Work

In order to estimate the impact of dechlorination processes on the New Bedford Harbor Superfund Site (NBHSS) and on lower New Bedford Harbor and to allow better assessment of remediation options, the following areas of research should be addressed:

1. Determination of the extent of dechlorination of PCBs at the highest concentration locations in the NBHSS. The data in this report show that dechlorination processes are more extensive as the concentration of PCBs in sediments increases. In this study, however, the highest PCB concentrations in sediment were approximately 3 parts per thousand. At some locations near the outfall of the Aerovox plant the PCB concentrations are in excess of an order of magnitude higher than those reported in this study. Detailed analyses of the composition of PCBs present in sediments from these hotspot locations should be done to determine the extent of dechlorination which has occurred.

2. Studies should be conducted to determine the rates of dechlorination processes to allow predictions of the types and quantities of PCB which will be present in the future if no remediation of the NBHSS is undertaken.

3. The toxicity of residues following dechlorination should be examined to allow evaluation of potential environmental benefits associated with these processes.